

193 nm Photodissociation of Thietane Probe via Synchrotron Radiation

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INTRODUCTION

Sulfur is abundant on the Martian surface.¹ It may also play an important role in the atmospheric sulfur cycle and could contribute to acid rain and atmospheric aerosols. Thietane (C₃H₆S) is a symmetric four-membered ring. Photolysis studies of thietane at different wavelengths were done by several groups.²⁻⁷ The CH₂S and C₂H₄ were identified as the major channel in previous photolysis studies.

The ionization potential is 9.21 eV and 10.36 eV for S(³P) and S(¹D), respectively. Therefore, in this study the S(¹D) atom can be selectively ionized by using tunable VUV light at 9.6 eV, whereas contributions from both S(³P) and S(¹D) can arise at energy of 10.7 eV.⁸ This method was applied to distinguish S(³P) and S(¹D) successfully in our previous studies of ethylene sulfide and propylene sulfide at 193 nm excitation.^{8,9} We report here the use of tunable synchrotron undulator radiation on the Chemical Dynamics Beamline of the Advanced Light Source, to probe selectively the singlet and triplet sulfur atom products, as well as other channels of the photodissociation of thietane at 193 nm. Four primary dissociation channels were observed: S + C₃H₆, HS + C₃H₅, H₂S + C₃H₄, and CH₂S + C₂H₄. But evidence suggested that only S(¹D) was formed for the sulfur atom loss channel.

EXPERIMENTAL SETUP

The experiments were performed on beamline 9.0.2.1 of the Advanced Light Source using a rotatable source molecular beam apparatus described in detail elsewhere.¹⁰ Helium was bubbled through a thietane sample at room temperature (~98% purity purchased from Fluka). The total pressure was about 800 Torr. The mixture of C₃H₆S and He was fed through a pulsed piezovalve into the main chamber. The resulting molecular beam was collimated with two skimmers, and the beam parameters were accomplished via the hole-burning technique at the parent ion mass (*m/e* = 60). The molecular beam was intersected at 90° with an ArF excimer laser beam. 15.2 cm downstream photofragments entering the triply differentially pumped detector region (~6×10⁻¹¹ Torr) were photoionized using tunable synchrotron radiation. This undulator light source discussed in detail elsewhere,¹¹ has a flux of 10¹⁶ photons/sec (quasi-continuous) and an energy bandwidth of 2.2%. A gas filter filled with about 25 Torr Ar was used to eliminate higher harmonics of the undulator radiation.¹² A MgF₂ optical filter was also used to eliminate small contamination of the probe light by higher energy photons when the probe energy was below 11.0 eV. The photoionized products were mass selected by a quadrupole mass filter, and were counted as a function of time-of-flight (TOF) with a Daly ion counter. The tunability of the VUV light source allowed for the measurements of photoionization efficiency (PIE) spectra. A series of TOF spectra, recorded at a fixed angle for different photoionization energies, were normalized for the probe photon flux, and integrated to obtain the PIE spectra.

RESULTS AND DISCUSSION

Four dissociation paths were observed from 193 nm photodissociation of thietane: $S + C_3H_6$, $HS + C_3H_5$, $H_2S + C_3H_4$, and $CH_2S + C_2H_4$. In this abstract, we focus on the $S + C_3H_6$ channel. Figure 1(a and b) show TOF spectra of $m/e = 32$ (S) at scattering angles of 15° and 30° with a probe photon energy of 9.6 eV, which is below the IP of $S(^3P)$. Hence, the data of $m/e = 32$ corresponds to the excited state $S(^1D)$. A translational energy distribution, shown in figure 1(c), was used to fit the data very well. The maximum translational energy extends out to 30 kcal/mol with a peak of roughly 5 kcal/mol.

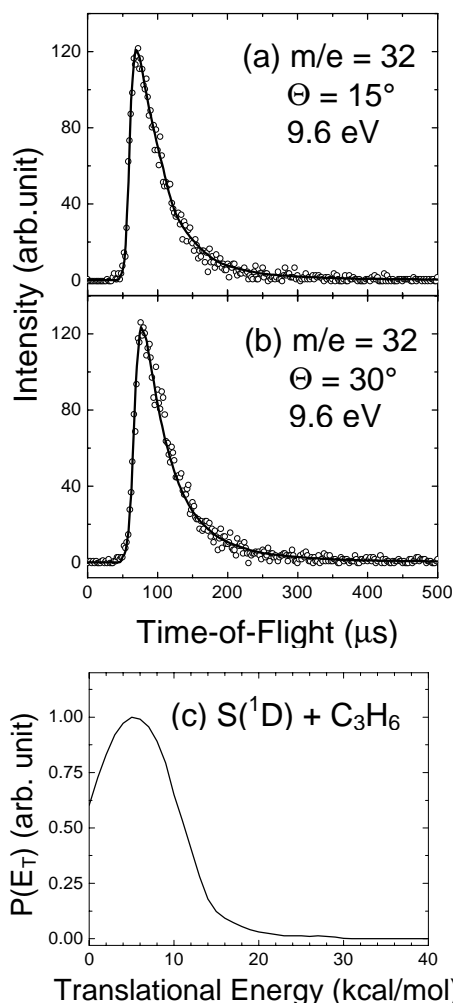


Fig. 1 (a) and (b) TOF spectra of $m/e = 32$ at 9.6 eV probe photon energy and scattering angles of 15° and 30° , respectively. (c) Translational energy distribution for the $S(^1D) + C_3H_6$ channel.

Fig. 2 shows the TOF spectra of $m/e = 32$ at 15° and the indicated photon energies. It is very clear that three TOF spectra are identical with the probe photon energy below and above the IP of $S(^3P)$. This means that the sulfur atoms are formed exclusively in the excited state, with no $S(^3P)$ contribution from thietane photodissociation at 193 nm. Photodissociation of most sulfides gives the mixtures of $S(^3P)$ and $S(^1D)$, because the outermost orbital is almost nonbonding, which increases the probability of intersystem crossing, even for the simplest sulfides such as H_2S ¹³ and CS_2 ^{14,15}. But, it is very surprising that in thietane the sulfur atom is formed only in the excited $S(^1D)$ state via a singlet potential energy surface. The dissociation could proceed along the excited potential energy surface of thietane with two C-S bond ruptures at same time.

A low resolution photoionization efficiency spectra (shown in Fig. 3) of the $S(^1D)$ was obtained at the scattering angle of 15° . The onset is about 9.2 eV, which is close to the IP of $S(^1D)$. Three obvious peaks are located at 9.6, 10.7, and 11.9 eV, respectively. These peaks include a series of Rydberg transitions, but can not be assigned in our low resolution measurement. In fact, these peaks are in coincidence with those of $S(^3P)$,^{16,17} on the basis of the energy difference of 1.15 eV between $S(^1D)$ and $S(^3P)$. Furthermore, two dips at 11.05 and 12.3 eV are the Rydberg converging limits to higher $^2D^0$ and $^2P^0$ states, respectively.

In summary, tunable synchrotron radiation combined PTS technique gives direct evidence that the sulfur atom is formed exclusively in the sole excited state $S(^1D)$ from 193 nm photodissociation of thietane. The low-resolution photoionization efficiency curve was obtained, and it is comparable to previous measurement of PIE (3P). Experiment suggests that thietane is a suitable molecule to produce pure $S(^1D)$, which is interesting to for studying bimolecular reactions with excited sulfur atoms, for atomic physics, and from the point of view of theory.

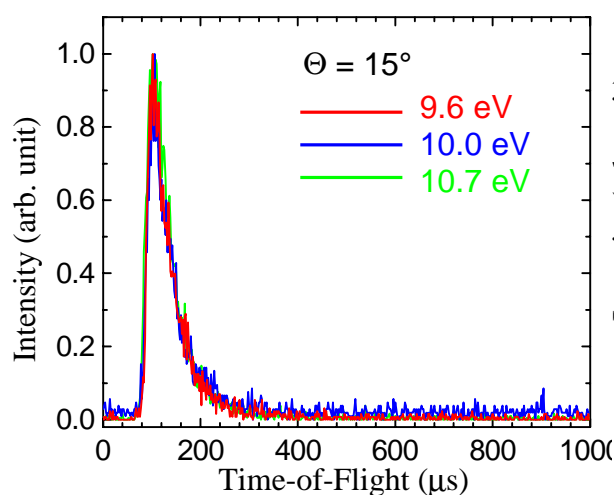


Fig. 2 TOF spectra of $m/e = 32$ at the indicated photon energies and 15° scattering angle.

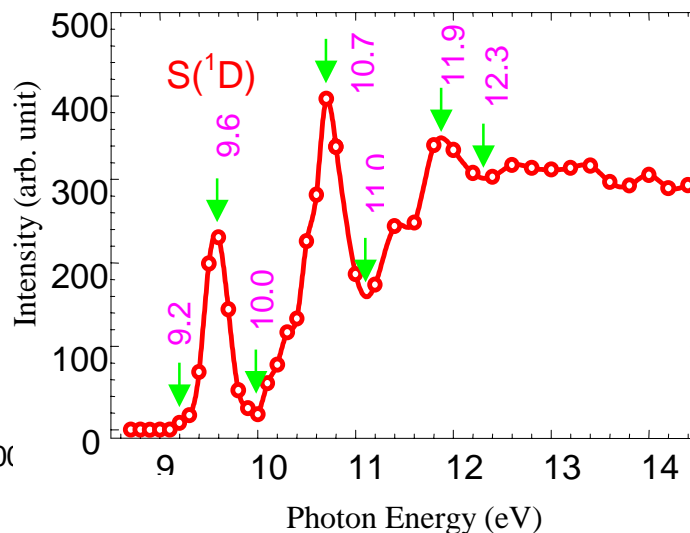


Fig. 3 Photoionization efficiency curve of $S(^1D)$.

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